

PATENT SPECIFICATION

NO DRAWINGS

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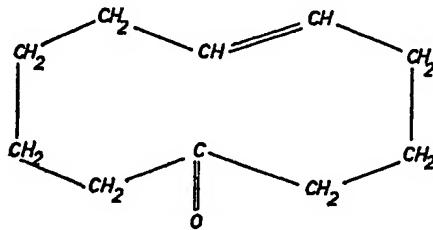
COMPLETE SPECIFICATION

Preparation of a Ketosebacic Acid

We GEIGY (U.K.) LIMITED, a British Company, whose Registered Office address is Simonsway, Manchester 22, Lancashire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to a process for the production of a derivative of a di-carboxylic acid and in particular to a process for the production of a derivative of sebacic acid.

15 According to the present invention, there is provided a process for the production of 5-ketosebacic acid which comprises treating cyclodec-5-enone having the formula:



20 with ozone and thermally oxidising the ozonised material at an elevated temperature.

25 The treatment of cyclodec-5-enone with ozone is conveniently effected by dissolving the cyclodec-5-enone in a solvent consisting of an aliphatic alcohol or monocarboxylic acid, the alcohol or acid being of straight-chain, and passing ozone into this solution. The alcohol or acid preferably contains from one to four carbon atoms and suitable alcohols are methanol and ethanol, whereas acetic acid and propionic acid are advantageously employed as acidic solvents.

[Price 5s. Od. (25p)]

The source of ozone in this process of the invention is preferably a stream of oxygen containing a minor proportion of ozone, for instance a proportion within the range of from 1.0% to 5.0% by weight.

35 The temperature at which the ozonisation procedure is conducted is preferably below 0°C. In this way volatilisation of the components of the reaction mixture is minimised. The ozonisation procedure is desirably carried out until all, or substantially all, of the ethylenically unsaturated double bond of the cyclodec-5-enone has been converted to the ozonide. The completion of the ozonisation reaction may be detected, for instance, by passing the effluent gases from the ozonisation reaction mixture through an aqueous solution of potassium iodid and boric acid, the precipitation of free iodine marking the completion of the ozonisation reaction.

40 The oxidative decomposition of the ozonide produced in the ozonisation stage of the reaction, is preferably effected at an elevated temperature by means of hydrogen peroxide in a fatty acid solution, for instance a formic acid solution of the ozonide. The oxidative decomposition of the ozonide may be effected, for instance, at temperatures up to the boiling point of the reaction mixture. If, however, hydrogen peroxide is employed as the oxidising agent in the decomposition procedure, the oxidative decomposition is conveniently effected by gently heating the reaction mixture until a vigorous exothermic reaction sets in. After this exothermic reaction has subsided, heating of the reaction mixture under reflux conditions for a short period of time, for instance, up to one hour, is usually sufficient to complete the oxidative decomposition.

45 55 60 65 70 The 5-ketosebacic acid so produced may be isolated, for example, by distilling off the

water and formic acid present in the reaction mixture, preferably under subatmospheric pressure. The solid product thus obtained may be further purified if desired by conventional means, for instance, recrystallisation from a suitable solvent such as ethyl acetate.

The cyclodec-5-enone starting material for 5-ketosebacic acid may be obtained, for instance, by pyrolysing 6-acetoxycyclodecanone or 6-benzoyloxycyclodecanone at elevated temperatures, preferably at a temperature in excess of 300°C. The pyrolysis is conveniently effected in the absence of added catalyst, in a reactor maintained at the desired temperature and fitted for distillation. The desired cyclodec-5-enone may be isolated after completion of the pyrolysis reaction by fractional distillation of the collected distillate.

Alternatively, the cyclodec-5-enone starting material may be obtained according to the procedure described and claimed in British Patent Specification No. 979,889 which employs a similar pyrolysis procedure but employs various metallic catalysts.

The acetoxy- and benzoyloxy-cyclodecanone are readily produced from 6-hydroxy-cyclodecanone by esterification processes, for instance, those described by R. Criegee, Berichte, 77B, 722, 1944.

The 5-keto sebacic acid produced according to the process of the invention is a useful intermediate in organic chemistry particularly for the production of sebacic acid which is an important industrial compound, especially in the form of its dialkyl esters. These esters find wide application both in the field of plasticisers for polyvinyl chloride and also as synthetic lubricants for modern turbo-jet aircraft engines. The production of sebacic acid from 5-ketosebacic acid is described and claimed in our copending British patent application No. 52602/66 (Serial No. 1196594).

The invention is further illustrated by the following Example. Parts and percentages therein are expressed by weight unless otherwise stated. Parts by weight bear the same relation to parts by volume as do kilograms to litres.

EXAMPLE 1

A. 27.4 parts of 6-benzoyloxycyclodecanone were added slowly to a reactor maintained at 400°C., and fitted for distillation. The 6-benzoyloxycyclodecanone was added over a period of 75 minutes. The distillate was taken up in ether, washed with dilute potassium hydroxide solution until free of benzoic acid, and then with water. Evaporation of the ether solution and distillation gave 13.8 parts of a fraction having boiling range 98° to 102°C. (12 millimetres of mercury pressure) and 1.2 parts of a residue. Gas/liquid chromatographical examination of the distillate showed that cyclodec-5-enone content was 85% by weight. (77% yield).

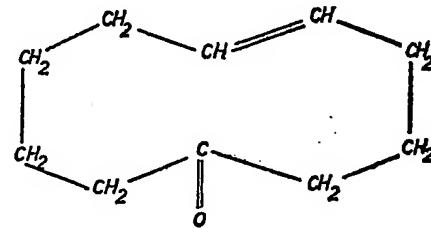
B. 15.2 parts of cyclodec-5-enone were dis-

solved in 100 parts by volume of methanol and treated with a stream of ozonised oxygen at -40°C., until the exit gases passing through an aqueous solution of potassium iodide and boric acid liberated iodine freely. The methanol solvent was then removed under reduced pressure leaving a viscous oil. To this oil was added 70 parts by volume of 90% formic acid and 20 parts by volume of 50% hydrogen peroxide. The reaction mixture was heated gently and after a few minutes a vigorous exothermic reaction set in. When this reaction has subsided, external heating at 100°C., was commenced for a further 15 minutes and finally the mixture was heated under reflux conditions for 30 minutes.

The reaction solvents consisting of water and formic acid were removed under reduced pressure leaving a solid residue which after recrystallisation from ethyl acetate, gave 10.4 parts of 5-ketosebacic acid having melting point of 115° to 117°C., representing a yield of 48% theoretical.

WHAT WE CLAIM IS:—

1. A process of producing 5-ketosebacic acid comprising treating cyclodec-5-enone having the formula:—



with ozone and thermally oxidising the ozonised material at an elevated temperature.

2. A process as claimed in Claim 1 wherein the ozonisation is conducted in the presence of a solvent consisting of an aliphatic alcohol or a monocarboxylic acid each being of straight-chain and having from 1 to 4 carbon atoms in the chain.

3. A process as claimed in Claim 2 wherein the alcohol is methanol or ethanol.

4. A process as claimed in Claim 2 wherein the acid is acetic acid or propionic acid.

5. A process as claimed in any of the preceding Claims wherein the cyclodec-5-enone is dissolved in the alcohol or acid solvent before being contacted with ozone.

6. A process as claimed in any of the preceding Claims wherein the ozone is in the form of ozonised oxygen.

7. A process as claimed in Claim 6 wherein the proportion of ozone in the ozonised oxygen is within the range of from 1% to 5% by weight.

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8. A process as claimed in any of the preceding Claims wherein the ozonisation is effected at a temperature below 0°C. 25

9. A process as claimed in any of the preceding Claims wherein the ozonisation is carried out until all or substantially all of the ethylenically unsaturated double bond in the starting-material has been converted to the corresponding ozonide. 30

10. A process as claimed in any of the preceding Claims wherein the oxidative decomposition of the ozonide is effected at an elevated temperature by means of hydrogen peroxide in a fatty acid solution of the ozonide. 35

11. A process as claimed in Claim 10 wherein the fatty acid solvent is formic acid. 40

12. A process as claimed in any of the preceding Claims wherein the oxidative decomposition of the ozonide is effected at a temperature up to the boiling point of the reaction mixture.

13. A process as claimed in any of Claims

10 to 12 wherein the oxidative decomposition of the ozonide is effected by gently heating the reaction mixture until a vigorous exothermic reaction sets in and, after the exothermic reaction has subsided, heating the reaction mixture under reflux conditions for a period of up to one hour.

14. A process as claimed in any of the preceding Claims wherein the 5-ketosebacic acid product is purified by removal of any solvent employed during the oxidative decomposition process.

15. A process of producing 5-ketosebacic acid substantially as described in the Example.

16. 5-Ketosebacic acid when produced by a process claimed in any of the preceding claims.

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